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SYNTHESIS OF PIGMENTS BASED ON THE $CuO - Cr_2O_3 - Al_2O_3$ SYSTEM USING THE PRECIPITATION METHOD

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Compositions of ceramic pigments for coloring glaze and flux coatings have been developed using the powder method and the coprecipitation method. Comparative parameters of chromophore properties of the obtained pigments are given. The expediency of using the coprecipitation method in the synthesis of ceramic pigments is demonstrated.

The purpose of the present work is to study a possibility of producing pigments based on $CuO - Al_2O_3$ and $CuO - Al_2O_3 - Cr_2O_3$ systems.

In the synthesis of pigments using the traditional powder method, Al_2O_3, Cr_2O_3, and CuO (analytical grade) were pulverized and fired in crucibles in a laboratory furnace at temperature 1100 C with holding at the maximum temperature of 30 min. For the purpose of comparison, pigments were obtained using the precipitation method. The authors used aqueous solutions of salts $Cu(NO_3)_2 \cdot 3H_2O$, $AlCl_3 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ (analytical grade, concentration 0.5 mole/liter), since in this case the use of ammonium solution would result in the formation of soluble ammonium copper complex. The obtained precipitate was filtered, dried, and fired. After firing, the pigment was pulverized until it passes through a No.0056 sieve with residue 0.5 – 1.5%.

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TABLE 1

Composition	Content of coloring components, mole		Firing results	
	CuO	Cr_2O_3	pigment	in glaze melt
1	1.00	–	Dark brown	Green
2	0.75	–	Brown	Turquoise
3	0.50	–	Coffee	Gray-turquoise
4	0.25	–	Brown	Whitish-sky-blue
5	0.13	–	Beige-brown	The same
6	0.88	0.07	Blackish-gray	Dark green
7	0.88	0.09	Black	The same
8	1.00	–	Dark gray	Bluish-green
9	1.00	1.00	Emerald	Gray
10	1.00	0.50	Emerald gray	The same

In order to test the pigments with respect to their color parameters, they were introduced into LG-10 fritted glaze in the amount of 3 – 10%. The glaze composition (wt.%) was as follows: 96 frit (LG-19), 2 – 4 Veselovskoe clay, and 0 – 2 kaolin. The following additives were introduced above 100%: 0.1 – 0.4 sodium nitrate, 0.03 – 0.1 sodium polyphosphate or tripolyphosphate, and 0.1 – 0.2 technical sodium carboxymethylcellulose. The moisture content in the glaze was 35 ± 2 wt.%

The pigment suspension was poured on the surface of facing tiles. The tiles were fired in a laboratory surface at temperature 950 ± 10°C with 30 min holding. After firing, the color of the pigment was visually determined (Table 1). The brightest were glaze coatings with pigments of compositions 1, 7, and 10.

The paste was prepared from flux based on LG-19 frit (45 – 55%) and transformer oil (45 – 55%0. The pigment was introduced in an amount up to 5% into the components metered in accordance with the formula. The resulting paste was applied to wet glaze and fixed in a two-tier roller furnace at temperature 890 ± 20°C.

The investigation results indicated that pigment 7 in the paste has a light-gray color, and pigment 10 has a greenish-gray color.

Since this technology for pigment production is very energy-consuming and involves high-temperature synthesis, mixtures were prepared by the coprecipitation method: composition 7′ and 10′, respectively, corresponded to compositions 7 and 10.

In order to determine the precipitation pH and the required amount of precipitator, pH-metric titration was performed on a EV-74 universal ionometer with glass (ESL-43-07) and silver chloride (EVL-1M3) electrodes. Based on the

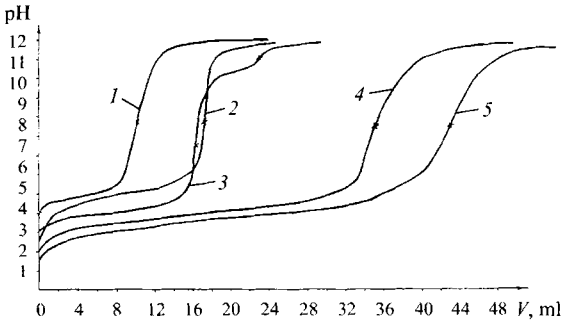

Fig. 1. Potentiometric titration curves: *1*) $Cu(NO_3)_2$ salt; *2*) $Cr(NO_3)_3$; *3*) $AlCl_3$ salt; *4*) composition 7'; *5*) composition 10'.

titration data, titration curves were constructed, and equivalence points were found from them (Fig. 1). One discontinuity can be identified on the titration curves of compositions 7' and 10', whereas the equivalence point of $Al(OH)_3$ dissolution (pH 12) is absent on the curves, which is evidence of a "loss of identity" of aluminum(III) in this precipitate. Copper hydroxide(II) in the precipitates is not dehydrated, i.e., copper also loses its "identity." This points to the fact that the resulting precipitate is not a mixture of individual hydroxides, but a hydroxide precipitate containing all three ions (Cu^{2+}, Al^{3+}, and Cr^{3+}). The completeness of precipitation was verified by qualitative reactions to ions Al(II), Cr(III) and Cu(II) in the filtrate. The specified ions were not identified in the filtrate. Therefore, quantitatively all of the ions pass to the precipitate.

The calculation showed that three titration discontinuities ought to be seen on the titration curve [1]. The absence of the second and third discontinuity is evidence of the fact that the precipitate is not a mechanical combination of hydroxides, but a chemical compound containing all three ions.

The required amount of precipitator was found from the titration curves. It was found that a slight excess of the precipitator, when pH of the mixture reaches 9.0 – 9.5, is sufficient.

The sequence of pouring solutions is of great importance for the precipitation method. That is why two precipitates of each composition were prepared, using both direct and reverse pouring of solutions. The precipitates matured in mother liquor for 3 days, then were filtered with subsequent washing of the precipitate on the filter to remove adsorbed Na^+, Cl^-, NO_3^- ions, since the latter degrade the properties of the product.

Next, the precipitates were dried and fired at temperature 1100°C. To determine their color parameters, the obtained pigments in specified quantities were introduced into fritted glaze LG-19 and paste. The results of firing of pigments obtained by coprecipitation are given in Table 2.

With the aim of attempting to combine the process of firing the precipitate and the process of fixing glaze on the crock, which would allow a significant saving in fuel, the behavior of non-fired precipitates in glaze melt and in paste was investigated as well.

On introducing fired pigments and non-fired precipitates in the glaze and paste, good colored coatings without visible defects were obtained.

The structure, phase composition, and color parameters of pigments synthesized using the powder technology and the coprecipitation method were investigated using differential thermal, thermodynamic, and x-ray phase analysis and the reflection spectra.

Study of the pigments produced on the basis of the powder technology indicated that there are three endothermic effects on the DTA curves of compositions 7 and 10 (Fig. 2). The first effect is related to the loss of nonstructural water (85 and 120°C, respectively), the second is associated with the loss of structural water (262 and 276°C), and the third is determined by the conversion of CuO to Cu_2O with formation of two-layer scale ($CuO + Cu_2O$; 865 – 983 and 895°C). The total weight loss in pigment 10 was 2.7%, and in pigment 7 it was 0.8%. When pigments are produced by the precipitation method, more substantial weight losses are registered. For direct pouring of solutions, the total weight loss in pigment 10' was 42%, in pigment 7' it was 35%, and for inverse pouring it was 40.75 and 37%, respectively. In this context, the yield of the end product was calculated. It was found that in the case of inverse pouring of solutions, the yield of the finished product is greater.

An analysis of DTA curves of the precipitates and individual hydroxides showed that they are not additive. Consequently, the obtained precipitates are chemical compounds containing Cr^{3+}, Cu^{2+}, and Al^{3+} ions.

Additional data on processes occurring in synthesis of pigments were obtained from thermodynamic calculations performed according to the method described in [2]. It was found that formation of spinels $CuO \cdot Al_2O_3$, $CuO \cdot Cr_2O_3$, and $CuO \cdot Cr_2O_3$ is possible in the given system. In this case,

TABLE 2

Composition*	Sequence of solution pouring	Color of obtained precipitate	Color of precipitate after firing	Color in glaze melt	Color in paste melt
		Fired pigments			
10'	Direct	Grayish-green	Black	Gray	Gray
	Inverse	The same	The same	Grayish-green	Dark gray
7'	Direct	Turquoise	The same	Green	Greenish-gray
	Inverse	Greenish-sky-blue	The same	Grayish-green	The same
		Nonfired pigments			
10'	Direct	Grayish-green	–	Gray	Grayish-green
	Inverse	The same	–	The same	Greenish-gray
7'	Direct	Turquoise	–	The same	Green
	Inverse	Greenish-sky-blue	–	The same	The same

* All compositions contained 5% pigment.

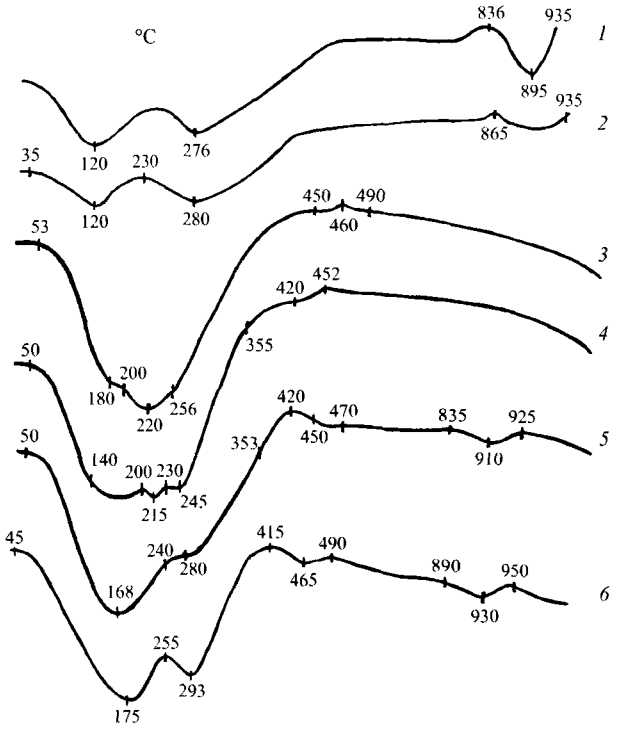

Fig. 2. Thermograms of pigments: *1*) composition 7; *2*) composition 10; *3*) composition 7′ (direct pouring of solutions); *5*) composition 10′ (direct pouring of solutions); *6*) composition 10 (inverse pouring of solutions).

TABLE 3

Composition*	Sequence of pouring solutions	Color coordinates			Color index coordinates		Color tone, nm	Saturation, %
		X	*Y*	*Z*	*x*	*y*		
Pigments obtained by powder technology								
10	–	14916	15613	14263	0.33	0.35	491	6
7	–	15860	17973	15636	0.32	0.36	497	8
Pigment obtained by coprecipitation								
10′	Direct	14511	15502	14285	0.33	0.35	491	6
	Inverse	17376	18773	15622	0.34	0.36	493	8
7′	Direct	16845	18443	16887	0.32	0.35	494	7
	Inverse	12431	13836	11757	0.33	0.36	499	9

* All compositions contained 5% pigments.

with increasing temperature, the probability of emergence of spinel $CuO \cdot Al_2O_3$ decreases, and that of emergence of $CuO \cdot Cr_2O_3$ and $Cu_2O \cdot Cr_2O_3$ increases.

The diffraction patterns of pigments produced by different methods exhibit reflections corresponding both to individual oxides (CuO, Al_2O_3, and CrO_3) and spinels ($CuO \cdot Cr_2O_3$, $CuO \cdot Al_2O_3$, and $Cu_2Cr_2O_4$). As the result of the x-ray phase analysis, it was established that a chemical compound, namely, a spinel, is formed regardless of the method of pigment synthesis, as could be expected. At the same time, the pigments contain a small quantity of free oxides. The pigments of composition 10′ contain a greater amount of spinel $CuO \cdot Al_2O_3$ and CuO, whereas composition 7′ contains more CrO_3 and $CuCr_2O_4$, which imparts a certain color to the synthesized pigment.

Reflections spectra were recorded on a SF-18 spectrophotometer SF-18 with a standard light source B. Chromaticity and color coordinates, saturation, and color tone were calculated by the method of [3]. The results of calculation are given in Table 3.

The color tone and the saturation of the composition 7′ pigments in glaze melt are higher than those of composition 10′. It was established that the predominant wavelength (or color tone) of the pigments and glaze coatings lies in the range of 487 – 550 nm. The presence of an indistinct maximum on the reflection curves is typical of green and gray pigments [4].

Thus, production of pigments by the precipitation method has certain advantages compared to the powder method. Synthesized pigments are recommended for production of colored glazes and pastes.

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